An unconventional Au/TiO_2 PROX system for complete removal of CO from non-reformate hydrogen

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Abstract

Au-based catalysts, generally known for high activity in the selective catalytic oxidation of CO to CO_2 at ambient temperatures, can play a significant role in increasing the fuel cell system's CO tolerance. In this work, an unconventional CO tolerance method, using an Au/TiO_2 "guard bed", has been investigated. The system is unconventional in the sense that it does operate as a PROX catalyst, but not in a traditional reformer system configuration. Instead, it has been developed to completely remove CO onboard the vehicle over a wide range, ppm to percentage levels, from impure pressurized H_2-rich gas, i.e. from partially enriched H_2 that would be stored in a fuel tank/cylinder but that would have some CO contamination and would essentially be dry. This set up will allow a reduction in the cost and complexity of conventional "off-board" hydrogen enrichment. The system CO tolerance obtained with the Au/TiO_2 system was compared with state of the art PtRu/C and PtMo/C CO tolerant anode technologies. Catalytic effectiveness in the removal of CO has been directly monitored by both direct analytical measurements and by monitoring the operation of a laboratory fuel cell to which the purified hydrogen stream was passed.

Keywords gold, titania, CO oxidation, hydrogen purification, CO tolerant fuel cell

1 Introduction

Some of the main challenges that remain for large scale fuel cell commercialisation include the purity, cost, and distribution of hydrogen. Hydrogen is currently the only practical fuel for use in present generation fuel cells. Pure hydrogen is attractive as a fuel because of its high theoretical energy density, its innocuous combustion product (water), and its unlimited availability as long as a suitable source of energy is available to decompose water via electrolysis. However, with current technology it is generally known that electrolysis is an uneconomical process of producing hydrogen. External processing of hydrocarbon compounds to yield a hydrogen-rich gas mixture seems to be a more viable method of producing large scale quantities of hydrogen in the foreseeable future. However, CO is a byproduct of the reforming process and has a well known poisoning effect on the Pt electrocatalyst at the anode and has to be removed to tolerable levels. High surface area PtRu electrocatalysts dispersed on carbon (PtRu/C) have shown enhanced CO tolerance [1 – 5]. Although less susceptible to CO poisoning, it has been shown that PtRu anodes are more likely to be poisoned by sulphur-containing gases such as H_2S and SO_2 than Pt anodes [6]. In addition, Oetjen *et al.* [4] reported a loss of 270 mV at 1 $A.cm^{-2}$ and 85°C for a PtRu/C electrode operating in CO concentrations of 100 ppm, which is still higher than that desirable for applications in a real system. Similar results were obtained by Ralph and Hogarth [5] who reported that even with an optimised $Pt_{0.5}Ru_{0.5}$ catalyst, the presence of 10 ppm CO significantly decreased the fuel cell's performance. Comparative data is given in Table 1 below:

Table 1

Progressive poisoning from 10, 40 and 100 ppm CO on pure Pt and Pt0.5Ru0.5 alloy anodes. Data obtained from [5]

CO (ppm in H_2)	mV at 0.5 $A.cm^{-2}$ over Pt	mV at 0.5 $A.cm^{-2}$ over PtRu
0	0.680	0.657
10	0.483	0.614
40	0.291	0.569
100	0.204	0.511

Even though the $Pt_{0.5}Ru_{0.5}$ anode showed increased CO tolerance at 0.5 $A.cm^{-2}$, the cell potential still decreased by 6.5% in the presence of 10 ppm CO, and 22.2 per cent in the presence of 100 ppm CO.

Another promising mixed metal anode is PtMo/C [7, 8]. Mukerjee *et al.* [9, 10] have shown a threefold increase in CO tolerance in commercial PtMo/C (E-TEK) in the presence of a mixture of H_2 and 100 ppm CO, with a loss of 100 mV at 1 $A.cm^{-2}$.

Although these materials show increased CO tolerance, a certain degree of performance loss still exists. In addition,

mixed metal anodes are more expensive than Pt/C anodes. Ideally, a system tolerant of CO concentrations in excess of 100 ppm, without a significant increase in the cost of the system and without any performance loss, is required for this technology to become industrially viable.

Au-based catalysts, generally known for high activity in the selective catalytic oxidation of CO to CO_2 at ambient temperatures, can play a significant role in increasing the fuel cell system's CO tolerance. In this work, an unconventional CO tolerance method, using a Au/TiO_2 "guard bed", has been investigated. The system is unconventional in the sense that it does operate as a PROX catalyst, but not in a traditional reformer system configuration. Instead, it has been developed to completely remove CO onboard the vehicle over a wide range, ppm to percentage levels, from impure pressurized H_2-rich gas, i.e. from partially enriched H_2 that would be stored in a fuel tank/cylinder but that would have some CO contamination and would essentially be dry. This set up will allow a reduction in the cost and complexity of conventional "off-board" hydrogen enrichment. The system CO tolerance obtained with the Au/TiO_2 system was compared with state of the art PtRu/C and PtMo/C CO tolerant anode technologies.

2 Experimental

2.1 Au/TiO_2 catalyst preparation

The Au/TiO_2 catalysts were prepared via deposition-precipitation, a preparation method known to yield nano-sized gold particles on the metal oxide support. The $HAuCl_4$ solution was added to high purity water that was preheated to 70°C, and the pH adjusted to 7.5 using 0.2 M Na_2CO_3, whereafter Degussa P25 TiO_2 was added as support. The catalyst was aged for 60 minutes at 70°C while maintaining the pH at 7.5 with 0.2M Na_2CO_3 and 0.2 M HNO3. The catalyst was washed in a five stage washing cycle with high purity water, where after it was filtered and dried at 120°C for 14 hours.

Cordierite ($Mg_2Al_4Si_5O_{18}$) monoliths (length = 7.6 cm; diameter = 1.5 cm; 400 channels/in^2) from Corning were used as the monolith structure to coat with Au/TiO_2 catalyst. The Au/TiO_2 nanopowder catalysts were prepared as mentioned above but were not dried at 120°C. In stead, the catalyst was re-slurried with high purity water to yield a catalyst slurry containing approximately 13wt% solids. The solids were kept in suspension by agitating with a magnetic stirrer. The monoliths were dipped into the catalyst slurry and soaked for 2 minutes, whereafter it was removed and the channels cleaned using slow-flowing compressed air. The Au/TiO_2 coated monoliths were dried at 120°C for 14 hours. The amount of catalyst deposited onto the monolith was determined by weighing the monolith before immersing into the catalyst slurry, and again after it was dried for 14 hours.

Transmission electron microscopy was used to characterize the gold dispersion in these systems, with catalyst being crushed between glass slides and dusted onto a carbon film supported by a copper grid. The samples were examined using a Tecnai F20 TEM.

2.2 Simulated Fuel cell operating conditions

The catalyst activity of the Au/TiO_2 catalysts was measured in the envisaged operating conditions in the onboard fuel cell system. The system was based on a Au-based catalyst chamber incorporated in the H_2 feed line prior to the anode humidifier. The simulation was based on a fuel cell system producing 60 kW at peak power. The required H_2 flow rate to deliver 60 kW was calculated using Equation 1.

$$Q = \frac{22.4141 \times mI}{n^{e^-} F} \quad (1)$$

where Q is the volumetric flow rate in cm^3 min^{-1}, 22.4141 is the volume of one mole of gas (dm^3.mol^{-1}), m a stoichiometric constant, I the drawn current in Amps (C.s^{-1}), n^{e^-} the moles of electrons transferred, and F Faraday's constant (96 485 C.mol$_e^{-1}$). Test work conducted during this investigation was based on a 1000x downscale of the actual fuel cell system. However, test conditions mimicked the actual space velocity as would be encountered in a full scale system.

Three different catalyst systems were investigated, namely 1) Au on P25 TiO_2 nano-powder, 2) Au on P25 TiO_2 granules (+500 -710 µm), and 3) Au on P25 TiO_2 nano-powder wash-coated onto cordierite monoliths.

2.3 System CO tolerance investigation

The efficiency of the Au/TiO_2 catalysts on the system's CO tolerance was tested in an actual fuel cell test system. The setup consisted of a catalyst chamber containing a Au/TiO_2 wash-coated monolith (length = 7.6 cm, width = 1.5 cm), situated at room temperature between the hydrogen cylinder and the anode humidifier, as depicted in Figure 13. The CO tolerance obtained with this system was compared to that of a 0.39 mg Pt.cm^{-2} Pt/C anode, a 0.5 mg Pt.cm^{-2} PtRu/C anode, and a 0.52 mg Pt.cm^{-2} PtMo/C anode.

Test work was conducted in a standard Johnson Matthey 49 cm^2 single cell PEM fuel cell system. The MEAs were conditioned at 0.5 A.cm^{-2} overnight. Hydrogen was introduced at 1.5 times the stoichiometric amount and air at 10 times the stoichiometric amount. The cell temperature was controlled at 80°C, while the humidifiers were set at 81.5°C and 82°C for the cathode and anode respectively. The heated lines to the fuel cell were controlled at 95°C.

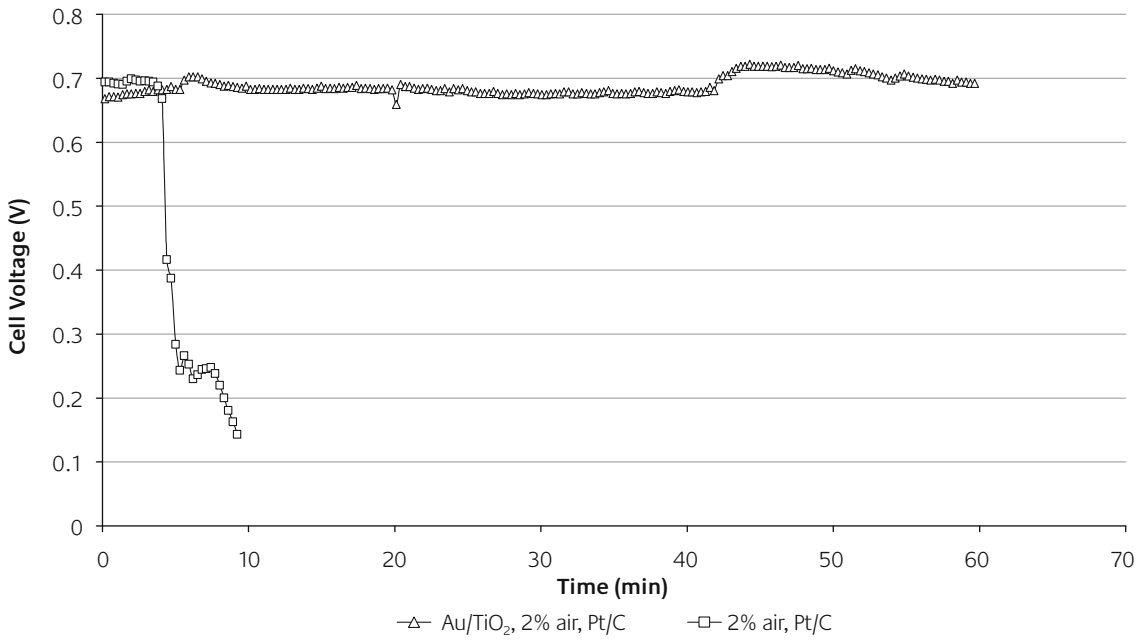
Once conditioned, and after the potential has stabilised, either 100 or 1000 ppm CO in H_2 was introduced to the anode, together with a 2 per cent air bleed stream. The cell potential was monitored for 1 hour where after the CO was removed. This process was done with and without the catalyst chamber containing the 3 wt% Au/TiO_2 PROX catalyst, and the CO tolerance of the various systems were compared.

In order to compensate for ohmic overpotential losses, the resistance compensated potential was determined by measuring the resistance by means of a current interrupt (CI) method, and subsequently adding the resistance-induced-potential-loss to the measured potential.

3 Results and discussions

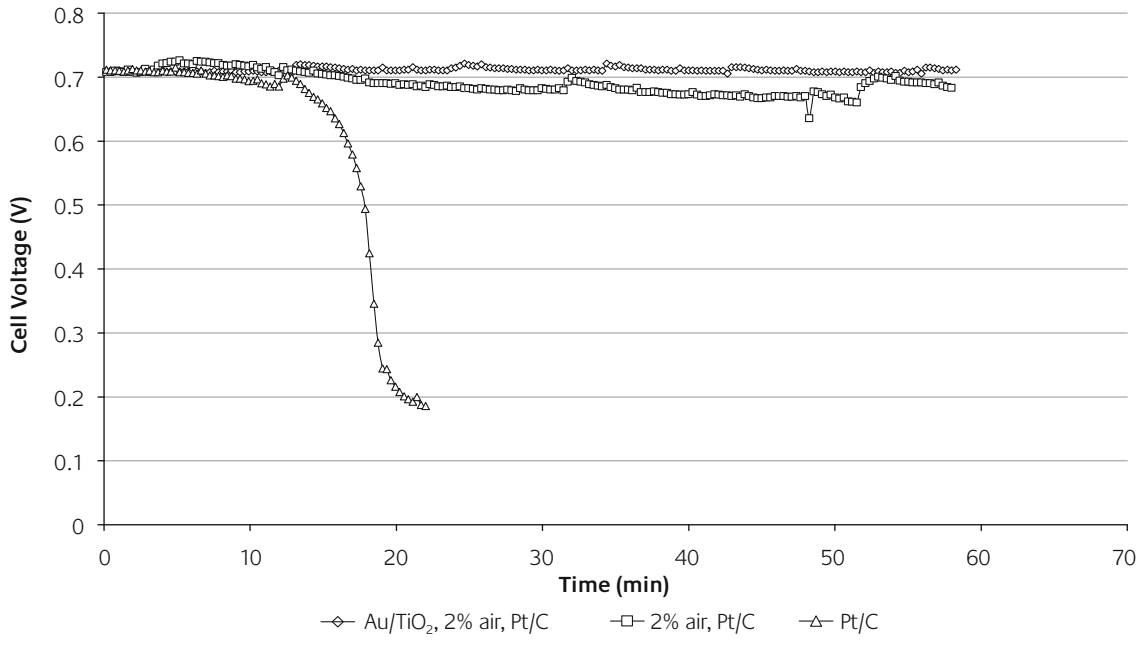
The TEM images showed that the gold particles (approximately 60 particles examined) were 2-3 nm in diameter and well dispersed. The dispersion was confirmed using high angle annular dark field (HAADF) measurements and particle

Figure 1



CO tolerance of a 0.39g Pt.cm^{-2} Pt/C anode with and without a 3wt% Au/TiO$_2$ coated monolith PROX reactor (1000 ppm CO, 0.5 A.cm^{-2}, 1.5x stoichiometric H$_2$ flow rate, SV over Au/TiO$_2$ catalyst 250 000 ml.g$_{cat}^{-1}$.h^{-1}, catalyst chamber at 25°C, cell temperature at 80°C, 0.84 mgPt.cm^{-2} Pt/C cathode)

Figure 2



CO tolerance of a 0.39 mg Pt.cm^{-2} Pt/C anode with and without a 3wt% Au/TiO$_2$ coated monolith PROX reactor (100 ppm CO, 0.5 A.cm^{-2}, 1.5x stoichiometric H$_2$ flow rate, SV over Au/TiO$_2$ catalyst 330 000 ml.gcat^{-1}.h^{-1}, catalyst chamber at 25°C, cell temperature 80°C, 0.84 mg Pt.cm^{-2} Pt/C cathode)

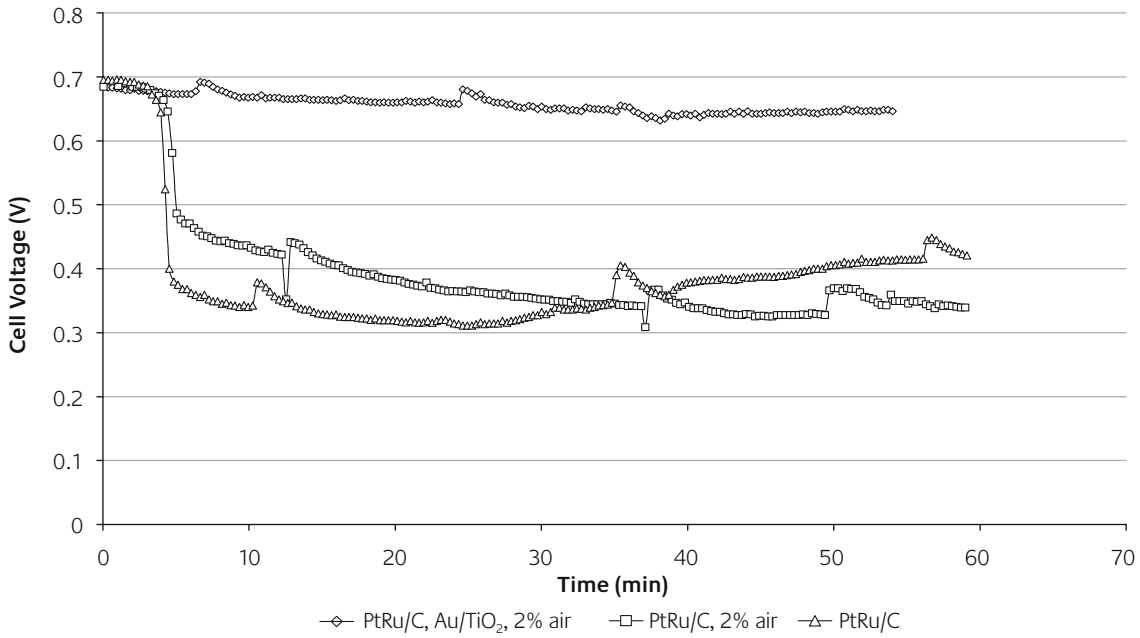
identification was accomplished using energy dispersive X-ray (EDX) analysis.

In the following sections the respective CO tolerances of Johnson Matthey Pt/C, PtRu/C, and PtMo/C anodes in 1000 and 100 ppm CO, with and without a 2 per cent air bleed, are reported. The influence of a 3 wt% Au/TiO_2 coated monolith PROX system on the CO tolerance of the system is also reported.

3.1 Pt/C

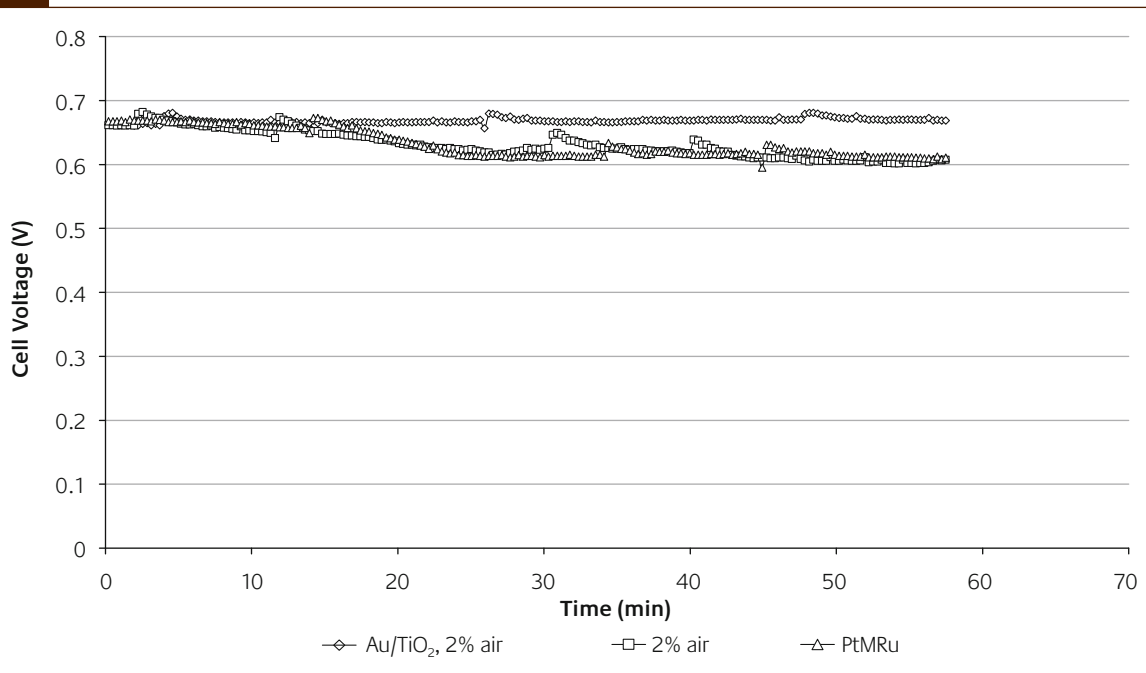
The influence of 1000 ppm CO with and without the Au/TiO2 PROX system on the performance of a 0.39 mg $Pt.cm^{-2}$ Pt/C

Figure 3



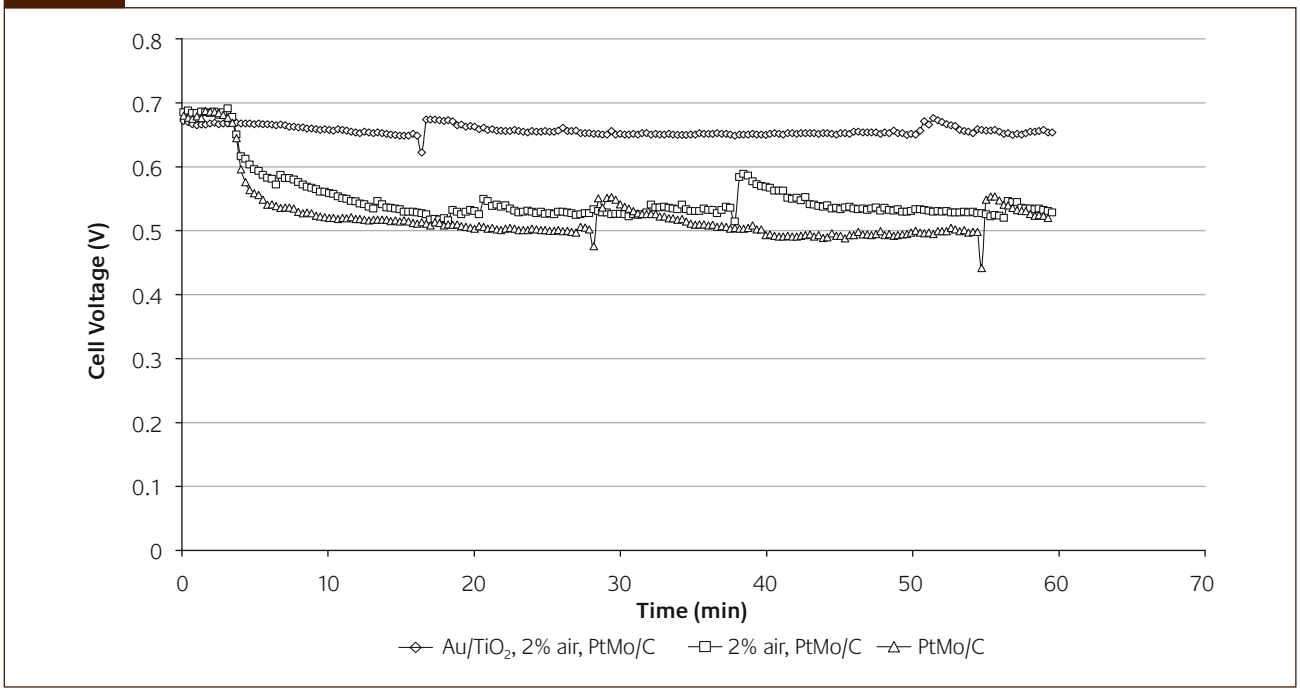
CO tolerance of a 0.5 mg $Pt.cm^{-2}$ PtRu/C anode with and without a 3wt% Au/TiO_2 coated monolith PROX reactor (1000 ppm CO, 0.5 $A.cm^{-2}$, 1.5x stoichiometric H_2 flow rate, SV over Au/TiO_2 catalyst 250 000 $ml.g_{cat}^{-1}.h^{-1}$, catalyst chamber at 25°C, cell temperature 80°C, 0.84 mg $Pt.cm^{-2}$ Pt/C cathode)

Figure 4



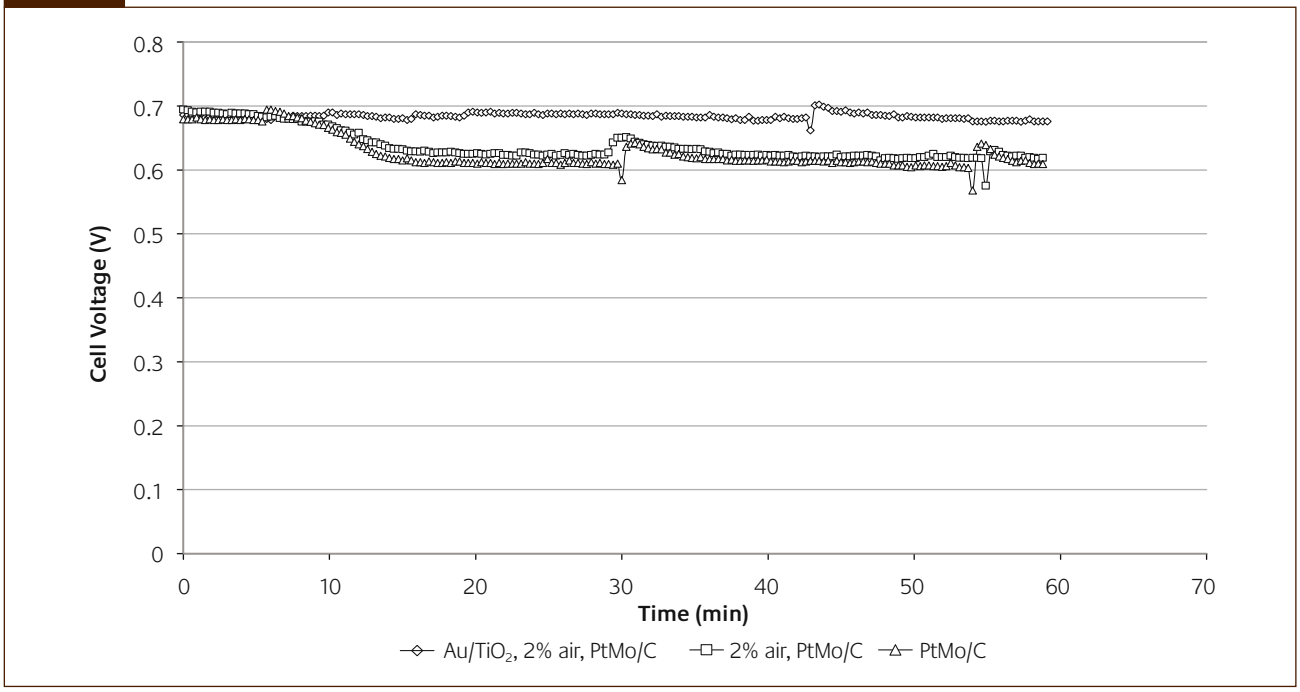
CO tolerance of a 0.5 mg $Pt.cm^{-2}$ PtRu/C anode with and without a 3wt% Au/TiO_2 coated monolith PROX reactor (100 ppm CO, 0.5 $A.cm^{-2}$, 1.5x stoichiometric H_2 flow rate, SV over Au/TiO_2 catalyst 330 000 $ml.gcat^{-1}.h^{-1}$, catalyst chamber at 25°C, cell temperature 80°C, 0.84 mg $Pt.cm^{-2}$ Pt/C cathode)

Figure 5



CO tolerance of a 0.52 mg Pt.cm^{-2} PtMo/C anode with and without a 3wt% Au/TiO$_2$ coated monolith PROX reactor (1000 ppm CO, 0.5 A.cm^{-2}, 1.5x stoichiometric H$_2$ flow rate, SV over Au/TiO$_2$ catalyst 250 000 ml.g$_{cat}^{-1}$.h^{-1}, catalyst chamber at 25°C, cell temperature 80°C, 0.84 mg Pt.cm^{-2} cathode)

Figure 6



CO tolerance of a 0.52 mg Pt.cm^{-2} PtMo/C anode with and without a 3wt% Au/TiO$_2$ coated monolith PROX reactor (100 ppm CO, 0.5 A.cm^{-2}, 1.5x stoichiometric H$_2$ flow rate, SV over Au/TiO$_2$ catalyst 330 000 ml.g$_{cat}^{-1}$.h^{-1}, catalyst chamber at 25°C, cell temperature 80°C, 0.84 mg Pt.cm^{-2} cathode)

anode is shown in Figure 1. As expected, the Pt/C anode did not show any tolerance against CO poisoning, even with the introduction of a 2 per cent air bleed stream. In contrast, no performance loss was observed over a 1 hour test period with the Au/TiO$_2$ PROX system prior to the fuel cell.

Figure 2 shows the influence of 100 ppm CO on the performance of the Pt/C anodes. The cell potential decreased due to poisoning in the absence of the PROX system and an air bleed stream. However, of interest is the fact that significant CO tolerance was obtained when a 2 per cent air bleed was introduced in the absence of the PROX system. This result is inconsistent with previously published results [5]. Also, when compared with the performance of PtRu/C in similar conditions (Figure 1) this result seems anomalous.

The presence of the Au/TiO_2 PROX system yielded superior results, as is evident from Figure 2.

3.2 PtRu/C

It is typically expected that PtRu/C anodes will yield better CO tolerance than Pt/C anodes. Again the influence of 1000 and 100 ppm CO on the electrochemical performance of the fuel cell with and without the Au/TiO_2 PROX system was investigated. The results are shown in Figures 3 and 4.

The 0.5 mg $Pt.cm^{-2}$ PtRu/C anode yielded significant CO tolerance compared to the Pt/C anode in the presence of 1000 ppm CO with and without an air bleed stream. Nevertheless, 1000 ppm CO resulted in a performance loss of 46 percent (356 mV) at 0.5 $A.cm^{-2}$. No significant effect was observed with the introduction of a 2 per cent air bleed stream. As in section 3.1 the presence of the Au/TiO_2 PROX system prevented any performance loss of the fuel cell.

Similar CO poisoning effects were observed on the PtRu/C anode when 100 ppm CO was introduced to the fuel cell. In this instance, approximately 9 per cent (67 mV) of the fuel cell's performance was lost due to CO poisoning. From Figure 4 it is evident that the Au/TiO_2 PROX system yielded superior results under these conditions.

3.3 PtMo/C

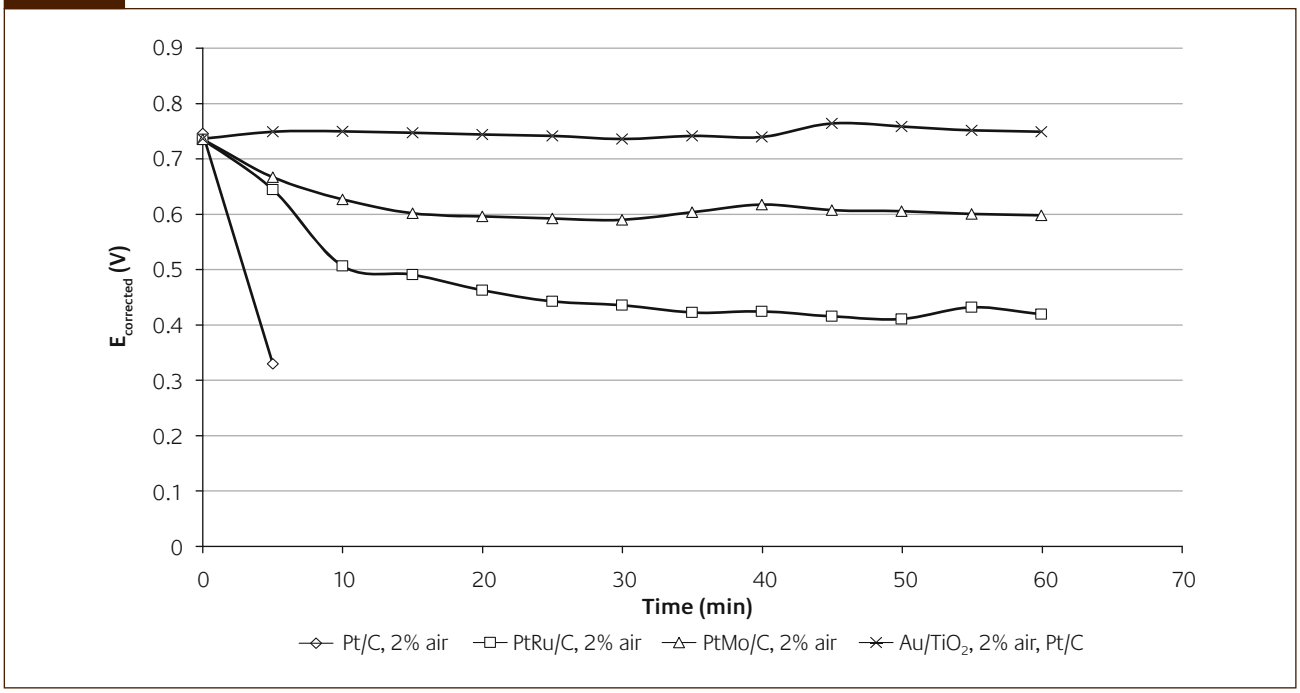
The results obtained for a 0.52 mg $Pt.cm^{-2}$ PtMo/C anode is shown in Figures 5 and 6. Even though PtMo/C offers improved CO tolerance compared with Pt/C and PtRu/C at higher CO concentrations, approximately 20% (153 mV) of the fuel cell's performance was still lost in the presence of 1000 ppm CO, and 9.2% (70 mV) in 100 ppm CO at 0.5 $A.cm^{-2}$ with or without an air bleed stream. The decrease in performance due to CO poisoning is significant and might influence the applicability of these catalysts in commercial fuel cell systems operating on contaminated H_2 gas streams. As in sections 3.1 and 3.2, the incorporation of a Au/TiO_2 PROX system was the superior method for CO removal / tolerance, as is evident from Figures 5 and 6.

A summary of the results are shown in Figures 7 and 8. The presence of the Au/TiO_2 PROX system in front of the Pt/C anode, the least CO tolerant anode, yielded superior results.

From the results discussed in sections 3.1, 3.2, and 3.3 it is evident that the Au/TiO_2 PROX system can act as a 'guard bed' in front of any fuel cell anode (Pt/C, PtRu/C, and PtMo/C) when CO is present (10 ppm – 1000+ ppm CO) in the H_2 fuel stream. For all the anodes investigated, the presence of the Au/TiO_2 PROX system eliminated the CO poisoning effect. These results are significant, since H_2 purity and the cost of H_2 to the end user are two of the main challenges for fuel cells to commercialize. The proposed Au/TiO_2 PROX system might therefore play an integral role in the pursuit towards large scale fuel cell commercialisation.

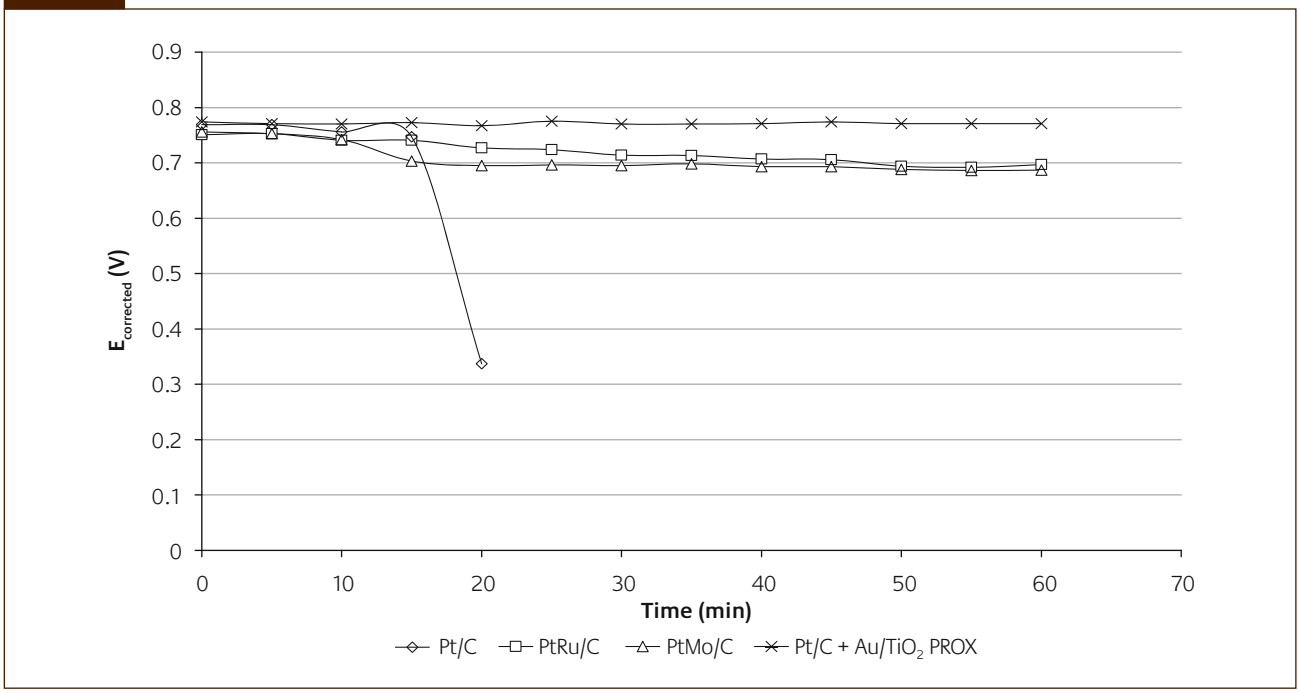
It is acknowledged that some further work is required in order to fully understand the long-term durability of the gold-based catalysts in complete CO removal in such systems [11,12].

Figure 7



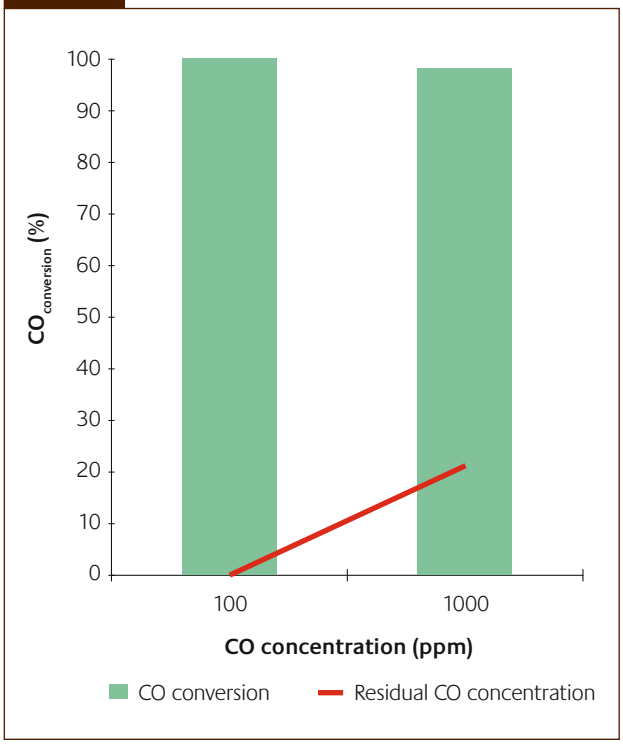
Summary of CO tolerance results (1000 ppm CO, 0.5 $A.cm^{-2}$, 1.5x stoichiometric H_2 flow rate, SV over 3 wt% Au/TiO_2 catalyst = 250 000 $ml.gcat^{-1}.h^{-1}$, catalyst chamber 25°C, fuel cell 80°C)

Figure 8



Summary of CO tolerance results (100 ppm CO, 0.5 A.cm^{-2}, 1.5x stoichiometric H_2 flow rate, SV over 3 wt% Au/TiO_2 catalyst = 330 000 ml.g_{cat}^{-1}.h^{-1}, catalyst chamber 25°C, fuel cell 80°C)

Figure 9



Removal of 100 or 1000 ppm CO from H_2 (2% air bleed, 330 000 ml.g_{cat}^{-1}.h^{-1}, 3 wt% Au/TiO2 coated monolith, 25°C)

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